

## Improvements in the Measurement of Distillation Curves. 2. Application to Aerospace/Aviation Fuels RP-1 and S-8<sup>†</sup>

Thomas J. Bruno\* and Beverly L. Smith

*Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80305*

In a previous paper, a number of improvements in the method and apparatus used for the measurement of distillation curves for complex hydrocarbon fluid mixtures were presented. These improvements included the addition of a composition-explicit channel of data, improved temperature control and measurement, and improved and less uncertain volume measurement. In this paper, we demonstrate the improved approach with application to two complex hydrocarbon fluids, rocket propellant 1 (RP-1) and a synthetic JP-8 that is designated as S-8. RP-1 is a long-established hydrocarbon fuel that continues to be widely used since it was first developed in the 1950s. Modern versions of this fluid are produced from a narrow-range kerosene fraction that is processed to reduce unsaturated compounds and also sulfur-containing hydrocarbons. S-8 is a synthetic substitute for fluids such as JP-8 and Jet-A. It is produced with the Fischer Tropsch process from natural gas. As these new and reformulated fluids gain increasing application, especially in aviation/aerospace application, it will be increasingly important to have material characterization test procedures that are reproducible and that have a sound and fundamental basis. This will allow modeling of the properties and guide further refinement of the fluids.

### Introduction

In the previous paper in this issue, improvements in the method and apparatus for the determination of distillation (or boiling) curves of complex hydrocarbon fluids were presented.<sup>1</sup> The major improvements included the introduction of a composition-explicit information channel, as well as improvements in temperature measurement and control, and improvements in volume measurement. In that paper, the many applications of the distillation curve were discussed; therefore such considerations will not be reproduced here. It is simply noted that because of the wide acceptance and importance of the distillation curve, it is clearly desirable to improve and extend the information that can be obtained from the measurement of it. This will advance the development of more refined testing procedures of lower uncertainty and will enable development of more advanced complex hydrocarbon fluids such as fuels.

In recent years, NASA and the United States Air Force have been interested in new aerospace fuels and in the reformulation of older such fuels. An example of an older fuel that has been reformulated in recent years is rocket propellant 1 (RP-1, MIL-P-25576C with amendment 2, CAS No. 52932-53-3).<sup>2</sup> This is a kerosene-like fluid that was used with liquid oxygen as the oxidizer on such vehicles as the Saturn V rocket engine (first stage). The recent desire for reformulation stems from the need to utilize rocket motors multiple times, rather than one time. The hydrocarbon fluid used for such motors must be very low in sulfur components, aromatics, and alkenic compounds. Distillates from crude oil that are high in paraffinic stocks are generally used for RP-1 production in order to meet specifications for density, heat of combustion, and aromatic content.<sup>3</sup> Previous analyses of RP-1 have shown the fuel to be a complex mixture of compounds including linear and branched paraffins, alkenes, and some aromatics.<sup>4–7</sup> Note that RP-1 in the context

of this work must be distinguished from dimethyl 4-cyclohexene-1,2-dicarboxylate, which is also referred to as RP 1 or RP 1 ester in the chemical literature.<sup>8</sup>

Environmental concerns, and the potential of disruptions in supply, have led to the development of new aviation fuels based on the Fischer Tropsch process. One such fuel made from natural gas is designated as S-8 (the “S” referring to synthetic; CAS No. 437986-20-4).<sup>9</sup> This fluid, which is intended as a synthetic JP-8, is a hydrocarbon mixture rich in C7 to C18 linear and branched alkanes. It has a flash point range of between 37.8 and 51.8 °C, an autoignition temperature of 210 °C, and explosive limits in air between 0.7 and 5 (vol/vol). It is clear in appearance (no dye is added to current formulations) and significantly lower in viscosity than RP-1.

### Experimental Section

The developmental apparatus used for the measurement of distillation curves of complex fluids has been described in detail earlier.<sup>1</sup> The major features of the apparatus include the addition of a compositional information channel that allows a chemical analysis to be done, on-the-fly, for any selected cut or point on the distillation curve. This was done with a receiver adapter equipped with a sampling area of known volume. Temperature control has been improved with the introduction of an aluminum enclosure that provides temperature uniformity in the horizontal plane, while allowing a controlled temperature gradient in the vertical direction. Observation of the fluid in the distillation flask and head is done in three locations of the apparatus with a flexible bore scope. Temperature is measured by thermocouples both in the fluid (which is the preferred location) and in the head (which is used for comparison to historical data). Fluid volume is measured with a level-stabilized receiver.

The fluids that were measured in this work, RP-1 and S-8, were obtained from the United States Air Force, Air Force Research Laboratory, Propulsion Directorate, and were used without treatment or purification. Care was taken to minimize exposure to the atmosphere, to minimize oxidation, evaporation of the more volatile components, and uptake of moisture.

\* To whom correspondence should be addressed. E-mail: bruno@boulder.nist.gov. Telephone: 303-497-5158. Fax: 303-497-5927.

<sup>†</sup> Contribution of the United States Government. Not subject to copyright in the United States.

**Table 1. Listing of the Components of RP-1 Identified by Gas Chromatography–Mass Spectrometry, Having Chromatographic Peak Area Counts in Excess of 1%<sup>a</sup>**

retention time, min	name	CAS reg no.	RMM	area %
8.268	2,6-dimethylnonane	17302-28-2	156.19	1.761
8.759	<i>x,y</i> -dipropylcyclopentane	NA	154.17	1.043
9.026	1-ethyl-2-propylcyclohexane	62238-33-9	154.17	0.0461
9.286	<i>trans</i> -decahydronaphthalene	493-02-7	138.14	1.402
9.598	2-methyldecane	6975-98-0	156.19	1.588
9.813	3-methyldecane	13151-34-3	156.19	1.260
10.824	<i>n</i> -undecane	1120-21-4	156.19	2.592
11.128	2-methyl- <i>trans</i> -decalin	1000152-47-3	152.16	1.355
11.373	2,6-dimethyldecane	13150-81-7	170.2	1.242
11.671	2- <i>syn</i> -methyldecalin	1000155-85-6	152.16	2.003
11.931	1,3-dimethylbutylcyclohexane	61142-19-6	168.19	1.364
12.703	5-methylundecane	1632-70-8	170.2	1.693
13.00	2-methylundecane	7045-71-8	170.2	2.287
13.223	5-ethyldecane	17302-36-2	170.2	1.384
13.714	1-methyl-1,2-pentylcyclohexane	54411-01-7	168.19	1.059
14.278	<i>n</i> -dodecane	112-40-3	170.2	2.351
14.754	2,6-dimethylundecane	17301-23-4	184.22	1.967
16.262	4-methyldodecane	6117-97-1	184.22	1.506
16.447	2-methyldodecane	1560-97-0	184.22	1.817
16.782	7-methyltridecane	26730-14-3	198.24	1.698
17.710	tridecane	629-50-5	184.22	2.585
17.978	1-methylnaphthalene	90-12-0	142.08	1.220
18.253	6-methyltridecane	13287-21-3	198.24	1.025
19.790	2-methyltridecane	1560-96-9	198.24	1.117

<sup>a</sup> The area counts are uncalibrated, and are intended only as a rough guide to the relative composition of the sample. In addition to the components listed here, there were two additional components in excess of 1% in area counts that could not be assigned by mass or infrared spectra.

The sample of RP-1 was pink in color because of the presence of a dye, azobenzene-4-azo-2-naphthol. This sample has been subjected to an extensive chemical analysis in previous work.<sup>10</sup> This work was done with a gas chromatography–mass spectrometry–infrared spectrophotometry method (30 m capillary column of 5% phenyl dimethyl polysiloxane, having a thickness of 1  $\mu\text{m}$ , temperature program from 90 to 250  $^{\circ}\text{C}$ , 10  $^{\circ}\text{C}/\text{min}$ ). Mass spectra were collected for each peak from 15 to 550 RMM (relative molecular mass) units, and infrared spectra were collected between 4000 and 600  $\text{cm}^{-1}$ . The assignment of major components (having an area percent in excess of 1%) are presented in Table 1. Overall, the sample of RP-1 showed approximately 350 peaks that could be easily distinguished from noise level and perhaps twice that number that were barely above noise level.

The sample of S-8 was analyzed with a gas chromatography–mass spectrometry method (30 m capillary column of 5% phenyl dimethyl polysiloxane having a thickness of 1  $\mu\text{m}$ , temperature program from 90 to 225  $^{\circ}\text{C}$ , 10  $^{\circ}\text{C}/\text{min}$ ). Mass spectra were collected for each peak from 15 to 550 RMM units. The sample of S-8 had fewer overall peaks, approximately 320 that were easily distinguishable from noise. The assignments of major components (having an area percent in excess of 1%) are presented in Table 2.

In addition to these analyses, a total sulfur analysis was done on both fluids with a gas chromatograph that was equipped with a sulfur chemiluminescence detector (SCD). Moreover, a copper strip corrosion test (CSCT) was done for each fluid. The results of the SCD and CSCT indicated that the samples were very low in sulfur. The results from the GC–SCD measurements showed that the sulfur peaks were nearly at the detection limit of the instrument/method, at 100 ppb (0.000 01 mol/(mol %)). Exposed copper strips were recovered from the CSCT indistinguishable from pristine strips. In addition to the chemical analysis work, the thermal decomposition of RP-1 fluid has been

**Table 2. Listing of the Components of S-8 Identified by Gas Chromatography–Mass Spectrometry, Having Chromatographic Peak Area Counts in Excess of 1%<sup>a</sup>**

retention time, min	name	CAS reg no.	RMM	area %
2.564	2,5-dimethylheptane	2216-30-0	128.26	1.071
2.803	4-methyloctane	2216-34-4	128.26	2.415
2.869	3-methyloctane	2216-33-3	128.26	1.251
3.123	<i>n</i> -nonane	111-84-2	128.26	1.534
3.757	4-methylnonane	17301-94-9	142.28	1.788
3.866	3-methylnonane	5911-04-6	142.28	1.307
4.186	<i>n</i> -decane	124-18-5	142.28	1.943
4.390	2,5-dimethylnonane	17302-27-1	156.31	1.106
4.820	5-methyldecane	13151-35-4	156.31	1.238
4.859	4-methyldecane	2847-72-5	156.31	1.068
4.902	2-methyldecane	6975-98-0	156.31	1.439
4.980	3-methyldecane	13151-34-3	156.31	1.488
5.312	<i>n</i> -undecane	1120-21-4	156.31	2.277
5.484	2,6-dimethyldecane	13150-81-7	170.31	1.191
5.664	4-ethyldecane	1636-44-8	170.33	1.077
5.906	5-methylundecane	1632-70-8	170.33	1.593
5.996	2-methylundecane	7045-71-8	170.33	1.007
6.074	3-methylundecane	1002-43-3	170.33	1.138
6.367	<i>n</i> -dodecane	112-40-3	170.33	2.434
6.524	<i>x,y</i> -dimethylundecane			1.730
6.926	2,4-dimethylundecane	17312-80-0	184.36	1.655
7.024	2-methyldodecane	1560-97-0	184.36	1.210
7.383	<i>n</i> -tridecane	629-50-5	184.36	1.630
8.306	<i>n</i> -tetradecane	629-59-4	198.39	1.289
8.396	<i>n</i> -pentadecane	629-62-9	212.41	1.114

<sup>a</sup> The area counts are uncalibrated, and are intended only as a rough guide to the relative composition of the sample. In addition to the components listed here, there was one additional component in excess of 1% in area counts that could not be assigned by mass spectra.

studied extensively,<sup>10</sup> thus ensuring that no unfavorable decompositions will affect the measurement of the distillation curve.

The composition information channels that were used in conjunction with the distillation curve measurements were provided by two separate chromatographic systems. These analytical systems differ from those used for the sample characterization in that they are optimized for quantitative, rather than qualitative analysis. Two gas chromatographs, one equipped with flame ionization (FID) and mass spectrometric (MS) detection, and the other equipped with sulfur chemiluminescence detection, were used. The method applied to the former instrument was as follows: 30 m capillary column of 5% phenyl dimethyl polysiloxane having a thickness of 1  $\mu\text{m}$ , temperature program from 90 to 250  $^{\circ}\text{C}$ , 10  $^{\circ}\text{C}/\text{min}$ . For the latter instrument, a short retention gap of approximately 1 m of uncoated fused silica tubing was connected between the injector and the sulfur chemiluminescence detector. What was desired here was a total sulfur analysis, rather than a separation or speciation into components.

Since the measurements of the distillation curve are performed at ambient atmospheric pressure measured with an electronic barometer, temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was done with the modified Sidney Young equation, in which the constant term was assigned a value of 0.000 109. This value corresponds to a carbon chain of 12. In the chemical analyses of the samples, as well as in previous work on these fluids, it was found that *n*-dodecane can represent these fluids as a very rough surrogate.<sup>11</sup>

## Results and Discussion

At the very start of measurement of the distillation curve, it is desirable to measure the initial boiling temperature with the bore scope approach described earlier.<sup>1</sup> For RP-1, three separate

measurements of the distillation curve were done, allowing three measurements of the initial boiling temperature. Bore scope observation allowed measurement of the temperature for the appearance of the first vapor bubble in the range of 190.2–201.9 °C, measured directly in the liquid. Stirring was momentarily stopped and then started again, as the observations were being made. This was necessary because the stirring action can entrain bubbles of air in the moving fluid and create the illusion of bubbling from nucleation sites. Sustained vapor bubbling in the distillation flask was observed in the range of 197.3–202.5 °C. Vapor was observed rising into the head when the temperature  $T_k$  reached a mean temperature of 202.7 °C, which is considered to be the initial boiling temperature for the mixture. The overall uncertainty of the initial boiling temperature for these three measurements was 0.02 °C. All of the uncertainties reported in this work are estimates of a combined expanded uncertainty with a coverage factor of 2 (that is,  $2\sigma$ ). These temperatures were measured at atmospheric pressure and are corrected with the modified Sidney Young equation, as discussed earlier, in which the constant  $C = 0.000109$  for an average carbon chain of 12 units.

For the S-8 mixture, the distillation curve measurement was performed three times at atmospheric pressure. The initial bubbling was observed in the range of 174.7–181.7 °C (corrected to 1 atm) for the three measurements. Bubbling was noted as being sustained in the range of 181.0 and 181.7 °C (corrected to 1 atm). Vapor was observed rising into the head at an average temperature of 182.0 °C (the initial boiling temperature at 1 atm), with a combined overall uncertainty of 0.1 °C.

A note about the temperature observations and uncertainties discussed above is in order to clarify the presentation of the temperatures. The initial bubbling temperatures and the sustained bubbling temperatures are provided as ranges observed in the individual measurements for each fluid. These measurements are necessarily somewhat subjective, especially for highly complex fluids. It is easy to miss the onset of very small bubbles or to mistake air entrainment (due to stirring the fluid just prior to an observation) for bubbling caused by a phase change. It is nonetheless important to make these observations, however, since many of these complex fluids show a period of initial bubbling, followed by a lull in bubbling, followed by the actual onset of boiling. There is overlap of some of the ranges quoted for the observation of the onset of bubbling and sustained bubbling. This simply results from differences observed in the three different samples. In contrast, the initial boiling temperature of the fluid is far less subjective; it is more easily recognized by the onset of the rise of vapor into the distillation head. This is a true state point that is better expressed as a mean and standard deviation with a coverage factor  $k = 2$ . The uncertainty in the atmospheric pressure measurement was 0.005 kPa. Thus, the overall uncertainties are a composite that encompass not only the random uncertainty of the temperature measurement but also the correction to atmospheric pressure, and minor variations in fluid composition caused by handling.

Tables 3 and 4 provide representative sets of distillation curve data for the fluids RP-1 and S-8, respectively. The temperatures are those measured directly in the stirred liquid. The observed temperatures,  $T_k^{\text{obs}}$  (at ambient pressure, noted in the table heading), and the temperatures that have been corrected to standard atmospheric pressure,  $T_k$ , with the modified Sidney Young equation are presented. The distillation curves for the fluids are presented in Figures 1 and 2, respectively, along with the composition channel information. Before treating the

**Table 3. Representative Data for the Distillation Curve Data of RP-1<sup>a</sup>**

vol fraction, %	$T_k^{\text{obs}}$ , °C	$T_k$ , °C
5	197.0	204.0
10	198.6	205.6
15	200.2	207.3
20	201.6	208.7
25	203.1	210.2
30	205.0	212.1
35	206.6	213.8
40	208.5	215.7
45	210.2	217.4
50	212.2	219.4
55	214.4	221.7
60	216.8	224.1
65	219.2	226.5
70	221.7	229.1
75	224.8	232.2
80	228.3	235.8
85	233.8	241.4
90	241.7	249.4

<sup>a</sup> The uncertainties are discussed in the Experimental Section of the text. Temperatures noted as  $T_k$  are corrected to standard atmospheric pressure with the modified Sidney Young equation. The actual observed temperatures are presented as  $T_k^{\text{obs}}$  and were measured at 82.96 kPa.

**Table 4. Representative Data for the Distillation Curve Data of S-8<sup>a</sup>**

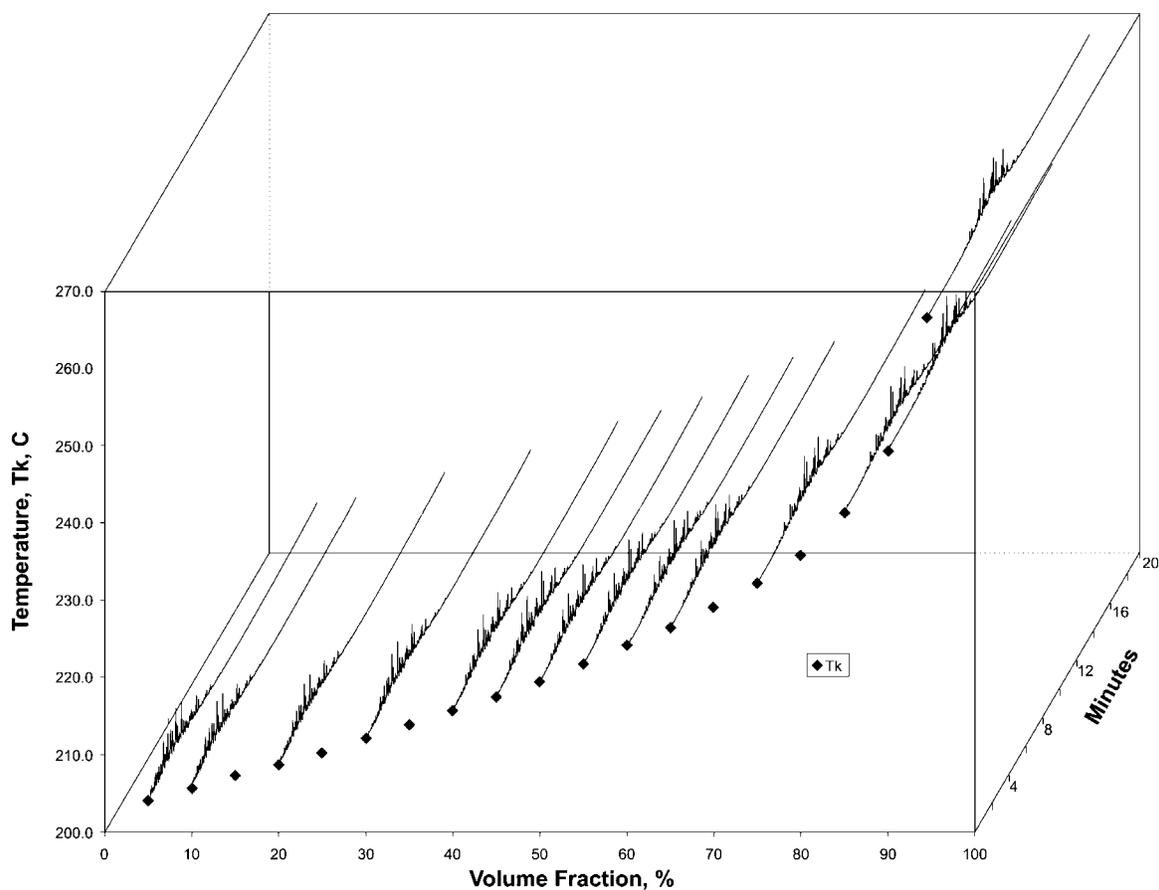
vol fraction, %	$T_k^{\text{obs}}$ , °C	$T_k$ , °C
5	178.7	185.2
10	181.2	187.8
15	184.0	190.6
20	187.0	193.7
25	190.2	196.9
30	193.4	200.2
35	196.7	203.5
40	200.8	207.7
45	204.6	211.5
50	208.9	215.9
55	213.3	220.3
60	218.0	225.1
65	222.8	230.0
70	227.8	235.1
75	233.5	240.8
80	239.2	246.6
85	246.1	253.6
90	253.7	261.3

<sup>a</sup> The uncertainties are discussed in the Experimental Section of the text. Temperatures noted as  $T_k$  are corrected to 1 atm with the modified Sidney Young equation. The actual observed temperatures are presented as  $T_k^{\text{obs}}$  and were measured at 83.27 kPa.

compositional information, we will first examine the gross structure of the temperature–volume fraction curves. The overall shape of the distillation curves is a subtle sigmoid, as would be expected for a complex mixture containing many components. In such cases, the sigmoid shape is far less pronounced than when fewer components are present that vary considerably in size and relative molecular mass. Difficulties with “hesitation”, which are commonly encountered when the temperature is measured in the distillation head (rather than in the fluid itself), are notably absent from these curves.<sup>12</sup> The reproducibility of distillation curves measured with the developmental apparatus is typically less than 0.5 °C. The reproducibility can be seen graphically in Figure 3, in which three separate distillation curves are presented for S-8.

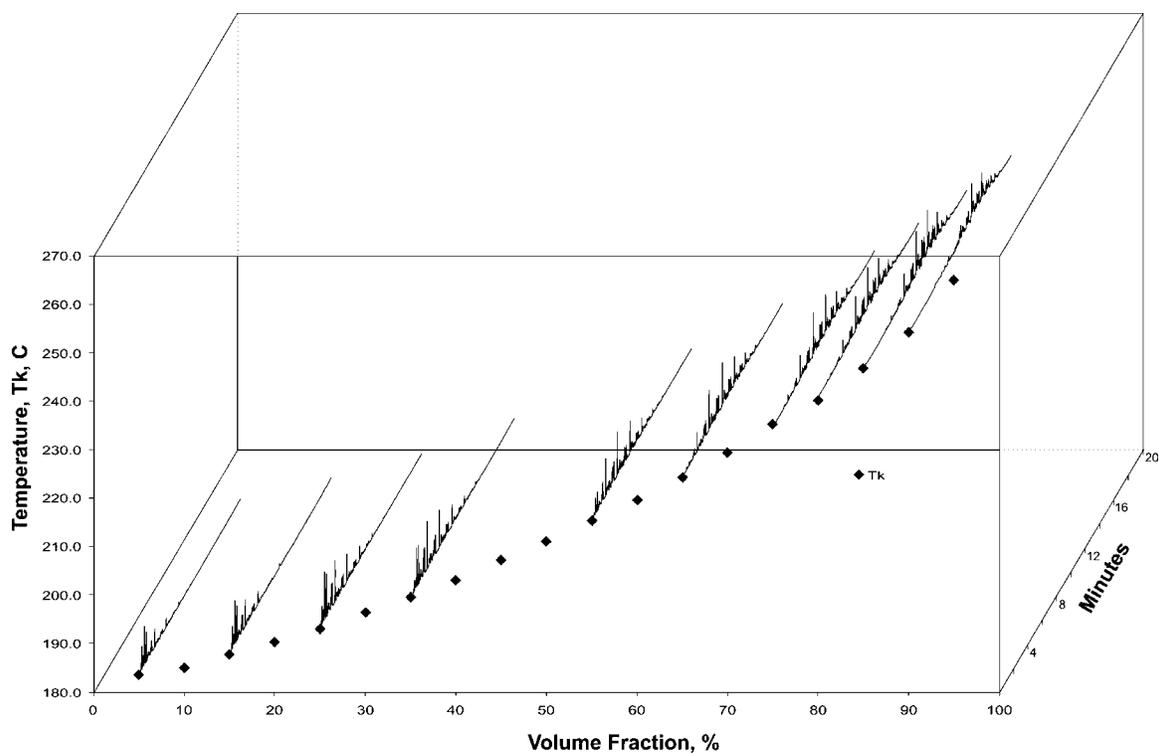
A thermocouple located in the distillation head of the developmental apparatus allows a comparison of distillation data taken with the new apparatus with historical data. This temperature is designated as  $T_h$ . Comparison is valuable in the developmental stage of the new apparatus not only because there is a large body of literature presented in this way but also because many fluid specifications are presented in terms of

## Distillation Curve for RP-1

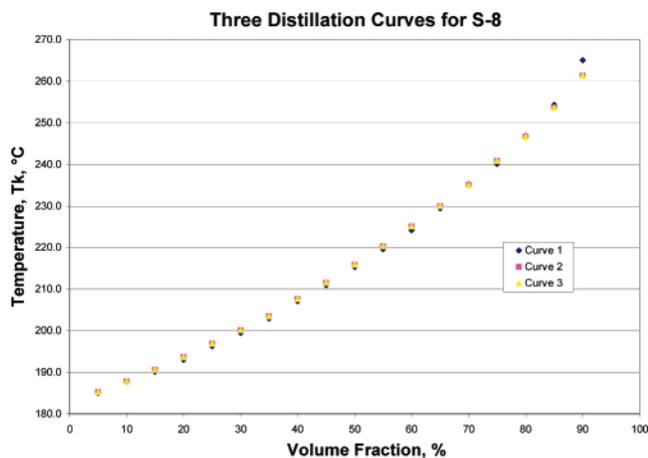


**Figure 1.** Representative distillation curve for RP-1 showing  $T_k$  against volume fraction in the  $x$ - $y$  plane, and the composition as measured by gas chromatography along the “ $z$ ” axis, represented as retention time against peak height (intensity). The uncertainties are discussed in the text.

## Distillation Curve 1 for S-8



**Figure 2.** Representative distillation curve for S-8 showing  $T_k$  against volume fraction in the  $x$ - $y$  plane, and the composition as measured by gas chromatography along the “ $z$ ” axis, represented as retention time against peak height (intensity). The uncertainties are discussed in the text.



**Figure 3.** Typical reproducibility of distillation curves measured with the developmental apparatus is illustrated by three separate curves measured for S-8.

**Table 5.** Comparison of  $T_h$  Values Measured in This Work, Relative to Historical Distillation Data of RP-1 and to Recent Data of S-8 with an Independent Measurement on the Same Lot

fraction	$T_h$ (°C)				
	NASA	CRC	AG	NIST	AFRL
(a) Historical Distillation Data of RP-1 <sup>a</sup>					
T10	185–210	197	$\delta$ 2.7	195.7	
T20			$\delta$ 2	199.0	
T50		205	$\delta$ 6	212.0	
T90		236	$\delta$ 6	241.0	
(b) S-8 with an Independent Measurement on the Same Lot <sup>b</sup>					
T10				179.0	169
T20				175.5	176
T50				205.2	201
T90				253.8	249

<sup>a</sup> The NASA specification is from ref 16; CRC is from ref 14, and AG is from ref 15. Because the original source of ref 13 is restricted, this comparison is presented as a deviation  $\delta$  from the NIST measured value.

<sup>b</sup> The source of the AFRL data is ref 17.

distillation head measurement. In Table 5a, a comparison is made between the  $T_h$  measured in this work (corrected to 1 atm with the modified Sidney Young equation) with available historical distillation data for RP-1.<sup>13–16</sup> In Table 5b, a similar comparison is presented for S-8, measured recently in an independent laboratory on the same lot of material.<sup>17</sup> The difference in the comparison stems from the long historical availability of RP-1, and the relatively recent availability of S-8. The data in these tables are presented as the common fractions used for specification purposes. Thus, T10 refers to the temperature at which the 10% volume fraction is observed, etc. For both RP-1 and S-8, the  $T_h$  measurements made in this work are very close to the historical measurements available for RP-1, and the previous measurements that are available for S-8. The typical deviation is approximately 5 °C, which is modest when one considers that fuel specifications often quote allowable temperature ranges of up to 25 °C.

The composition channel provides the chromatogram of each cut in the  $z$ -axis, as shown in Figures 1 and 2. In these figures, the chromatograms were measured with the GC-FID method described earlier. The gross structure of the chromatograms illustrate that the component suite for the early fractions is rich in very light components. As the distillation curve progresses to higher and higher volume fractions, the chromatograms show that the components that make up the fraction shift to longer retention times. Because of the nature of the stationary phase, one can observe that the chromatograms shift toward higher

**Table 6.** Comparison of an ASTM D-2789 Analysis for the First Drop and the Last Drop Recovered from the Distillation of RP-1<sup>a</sup>

sum	category	first drop	last drop	$\Delta$ , %
43	paraffins	27.0	36.4	+26
41	monocyclo-	43.4	34.7	-20
67	dicyclo-	18.6	20.1	+7.5
77	alkylbenzenes	10.2	6.1	-40
103	indanes	0.6	0.5	-20
128	naphthalenes	0.1	2.3	+96

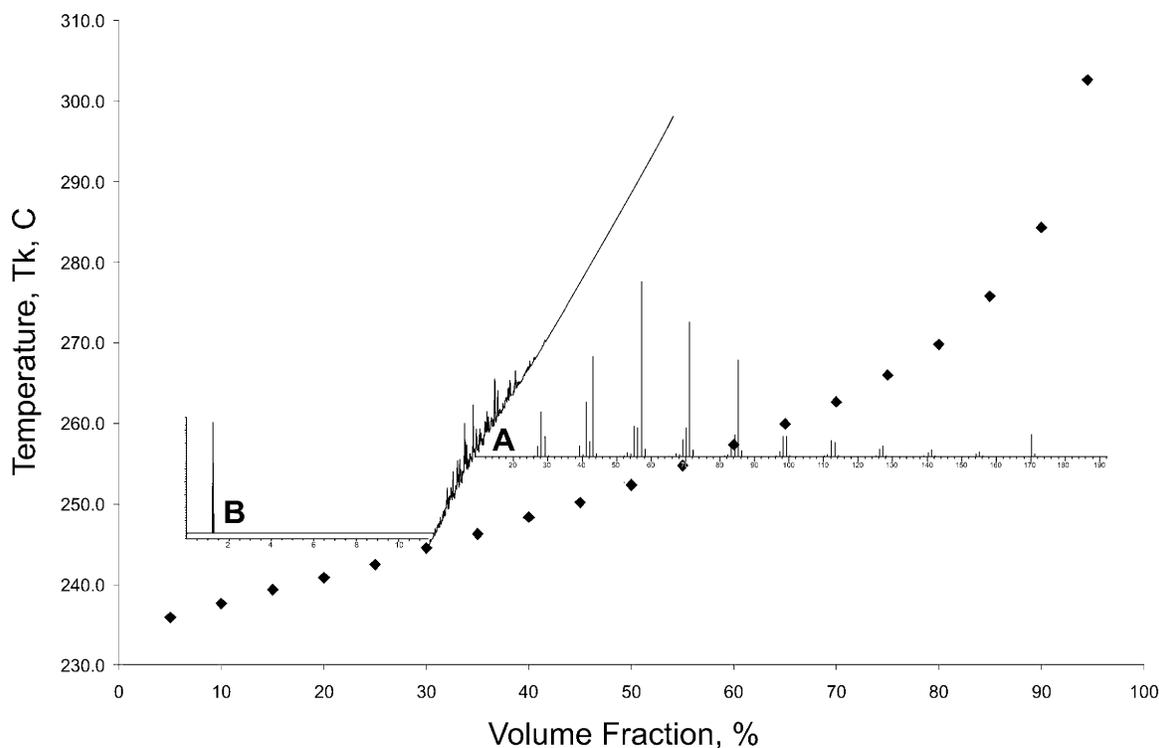
<sup>a</sup> The categories (and their related sum series from D-2789) are presented as volume fractions, along with the percent change from the first to the last drop.

boiling point components as the temperature of each cut increases. Having this presented as an on-the-fly chromatogram is advantageous in that one can relate the compound suite to the temperature on the distillation curve. The diagnostic value of this information will be illustrated later in this section.

The composition channel allows the application of any analytical method or technique that is amenable to a liquid organic sample in solution. This includes additional ASTM methods that are commonly applied to hydrocarbon fuels. One such method is D-2789, a gas chromatographic mass spectrometric technique that classifies hydrocarbons into families (paraffins, monocyclics, dicyclics, alkyl benzenes, indanes/tetralins, and naphthalenics). While not without its limitations, and certainly not the only such test used for gross characterization, it can be used reliably as a comparative tool, for evaluations between individual batches of fuels. The availability of D-2789 categorization for each distillate fraction (of the D-86 analysis) greatly expands the insight gained from either method used alone. We have applied the methodology of ASTM D-2789 to the first and last drops of fluid recovered from the distillation of the sample of RP-1. These data are presented in Table 6, in which the category fractions (and their related sum series) are presented as volume fractions, along with the percent change from the first drop to the last. While not all of the categories calculated by this method are applicable to RP-1, several are significant. These are the paraffins, alkyl benzenes, and naphthalenics; the others are often unreliable or insignificant in the analysis of samples such as RP-1. It is clear that there are major compositional changes in these categories from the first to the last drop of RP-1 distilled. The fractions of paraffins increase markedly, those of alkylbenzenes decrease markedly, and those of the naphthalenics increase dramatically. This is consistent with the implications of the distillation curve itself, and also with more detailed analyses that have been done.

Since the use of the sampling receiver adapter results in an aliquot that can be analyzed by any applicable technique, the information that can be augmented by the composition channel includes spectroscopic data and element selective detection. This may be illustrated by measuring the distillation curve of a sample of RP-1 that has been spiked with 1 ppm (mass/mass) of ethyl mercaptan. This curve is provided as Figure 4, in which the chromatogram (measured with flame ionization detection, FID) for the 30% fraction of the distillation curve of RP-1 is also shown. It can be seen from the appearance of the curve that this trace quantity of a sulfur compound makes no noticeable difference to the distillation curve. A separate analysis with a gas chromatograph equipped with a mass spectrometer was done on the sample from the 30% fraction and was matched (peak to peak) to the FID chromatogram. The mass spectrum of the major constituent, shown in inset A, can be identified as resulting from *n*-dodecane. Another analysis with a gas chromatograph equipped with a sulfur chemiluminescence detector is shown in inset B, in which a total sulfur analysis without

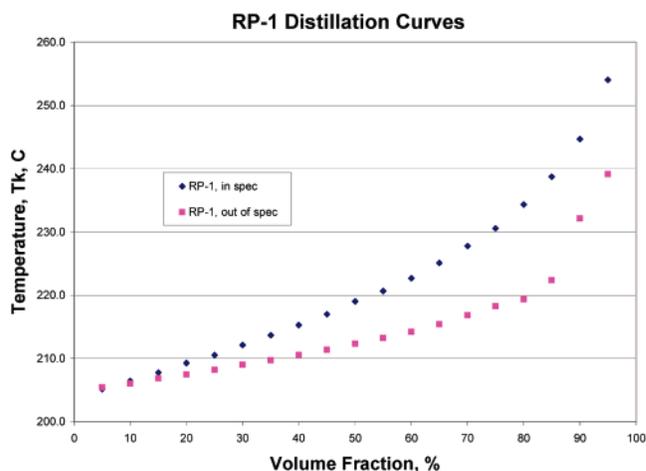
## Distillation Curve for RP-1



**Figure 4.** Distillation curve for RP-1, in which the chromatogram for the volume fraction at 30% is shown. Analytical samples were routed into a mass selective detector (inset A) and a sulfur chemiluminescence detector (inset B). The mass spectrum of the largest peak allows the identification of *n*-dodecane. The sulfur detector shows the presence of spiked ethyl mercaptan.

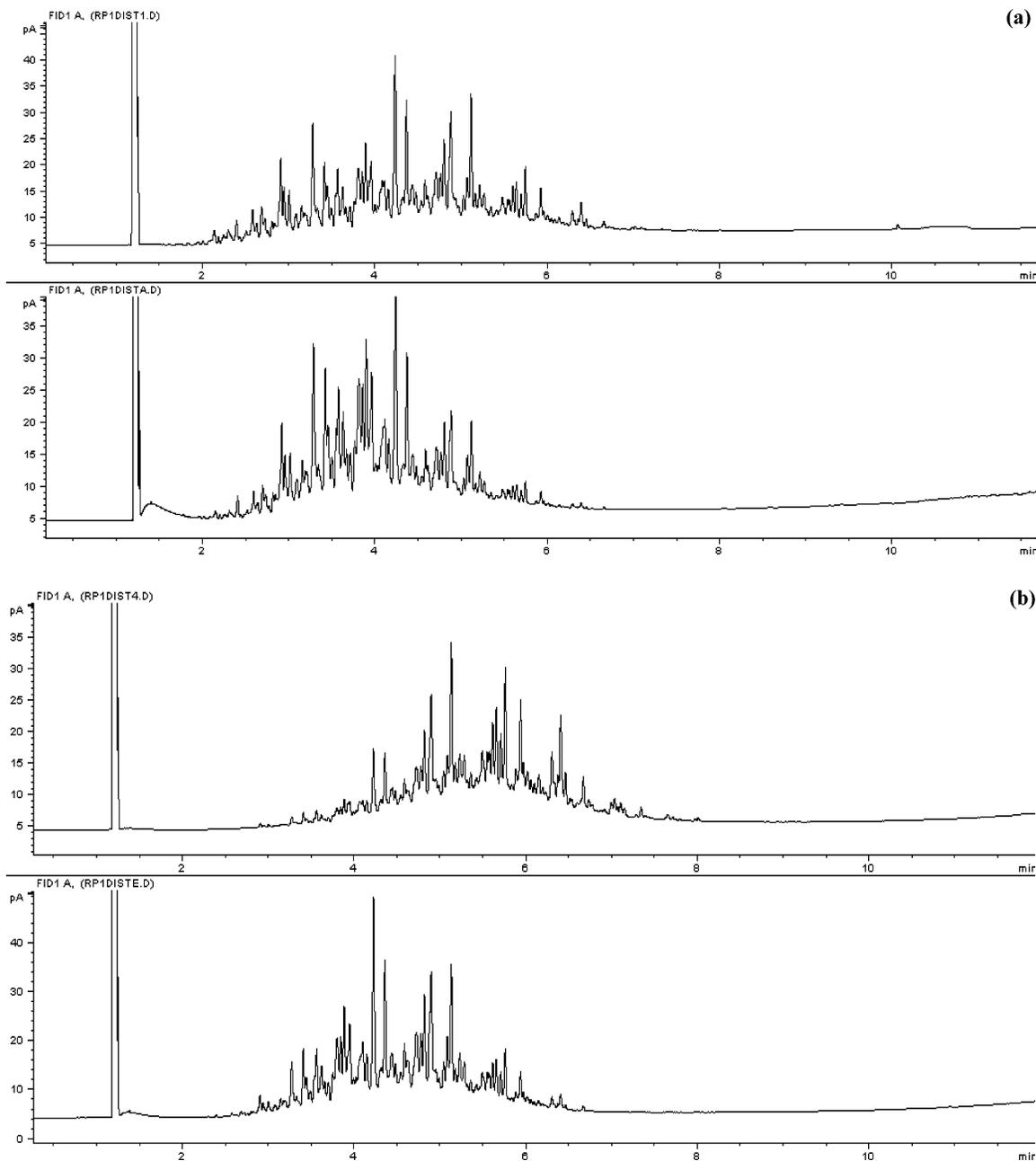
separation was performed. The chromatogram shows the response to the presence of ethyl mercaptan. This application of secondary, off-line analyses applied to distillation curve fractions can be very valuable for diagnostic purposes and to explain the structure of distillation curves. Moreover, it can be helpful in resolving discrepancies in such curves.

As an illustration of the application of the composition channel in resolving discrepancies in distillation curve data, one can compare the measurement of RP-1 considered earlier (Figure 1, Table 3) with measurements performed on an off-specification lot of the same material. As part of a large program on the thermophysical properties of RP-1 recently completed at NIST, it was discovered that one of the samples of RP-1 was unusual in that it had a larger than expected concentration of aromatic and alkenic constituents.<sup>18</sup> The within specification batch had markedly fewer aromatic and alkenic compounds, instead being much richer in saturated branched aliphatics. The unusual composition of the out of specification batch was reflected in numerous property measurements such as density, viscosity, and thermal decomposition rate constants.<sup>19</sup> The viscosity of the RP-1 that was within specification was between 4 and 9% higher than that of the off-specification batch. The decomposition rate constants of the within-specification batch were lower. These observations are consistent with the difference in composition. In addition, differences were noted in the distillation curves of the two different batches of RP-1. Since it would be of value to employ the composition channel to resolve and understand such differences, the distillation curves of samples from each batch were measured. These curves are presented in Figure 5, which shows the pronounced divergence at the heavy part of the curve. The overall structures of the curves are consistent with the property measurements; the out-of-specification batch is lighter in the higher volume fraction range of the distillation curve than is the within-specification batch. Analytical samples



**Figure 5.** Distillation curves for a sample of out-of-specification RP-1 and a sample that is within specification.

were drawn at volume fractions of 70, 80, 90, and 95% and were dissolved in *n*-hexane solvent. These samples were analyzed by a gas chromatographic FID method similar to that described earlier. The major difference in the analytical method was the application of a pressure-pulsed splitless injection sequence consistent with chromatographic trace analysis. Representative chromatograms for the 70 and 90% fractions are shown in Figure 6a,b. The greater preponderance of chromatographic peaks at the later eluting stage of the chromatograms of the within specification fluid is clearly visible. Analysis by a gas chromatographic mass spectrometric method confirmed that these additional peaks in the heavier fractions of the two fluids are indeed saturated branched aliphatic compounds. Moreover, there is a correlation in the appearance of the chromatograms and the disparity (or distance, in °C) in the



**Figure 6.** Chromatograms for the (a) 70% fraction and (b) 90% fraction of in-specification (top) and in-out-of-specification (bottom) RP-1. The large peak on the extreme left is that of *n*-hexane, the solvent.

distillation curves. As the divergence between the two curves becomes more pronounced, one finds more later-eluting peaks on the corresponding within-specification chromatograms. Thus, the composition channel aids in explaining the structure of the curves.

### Conclusions

The application of a developmental distillation curve measurement apparatus and method to complex fluids (real fuels) has been illustrated. The value of a compositional information channel has been demonstrated with a rocket propellant, RP-1, and a synthetic aviation fuel, S-8. The compositional information allows an explicit correlation of the structure of the distillation curve to the fractional composition of each fluid. Moreover, the advantages of measuring the temperature directly in the well-stirred fluid, instead of the head, have been discussed. Finally,

it has been demonstrated that the compositional information channel is important in explaining unusual or disparate results that might result from off-specification batches of fluids.

### Acknowledgment

Helpful discussions with Marcia Huber, Eric Lemmon, and Mark McLinden of NIST are gratefully acknowledged. One of us (B.L.S.) acknowledges the Professional Research Experience Program (PREP) of NIST for an undergraduate fellowship. We also acknowledge the assistance of Esther Nakagawara, a Summer Undergraduate Research Fellowship (SURF) student at NIST during the summer of 2005, for work on the ASTM-D-2789 characterization. The financial support of the United States Air Force, Air Force Research Laboratory, Propulsion Directorate (Grant MIPR NGWSPR00472412) is gratefully acknowledged.

## Literature Cited

- (1) Bruno, T. J. Improvements in the measurement of distillation curves. I. A composition-explicit approach. *Ind. Eng. Chem. Res.*, previous paper in this issue.
- (2) Ma, H. A study on thermal stability and its improvement of hydrocarbon fuel. *International Annual Conference of ICT*; 1993; Vol. 24; pp 88–81/88–12.
- (3) Military Specification MIL-P-25576C, U. S. M., 1967.
- (4) Farmer, R. C.; Anderson, P. G.; Cheng, G. C.; Myruski, B. L.; Pike, R. W. Propulsion chemistry for CFD applications, Contract No. NAS8-40574 Final Report; National Aeronautics and Space Administration: Washington, DC, 1997.
- (5) CPIA/M4, L. P. M.; Chemical Propulsion Information Agency: Laurel, MD, 1997.
- (6) Edwards, T. “Real” kerosene aviation and rocket fuels: Composition and surrogates. *Chemical and Physical Processes in Combustion*; 2001; pp 276–279.
- (7) Edwards, T.; Maurice, L. Q. Surrogate mixtures to represent complex aviation and rocket fuels. *J. Propul. Power* **2001**, *17*, 461–466.
- (8) Aldrich Chemical Co., S. c., 2005.
- (9) MSDS S-8 synthetic jet fuel, material safety data sheet; Syntroleum Corp.: Tulsa, OK, 2005.
- (10) Andersen, P. C.; Bruno, T. J. Thermal decomposition kinetics of RP-1 rocket propellant. *Ind. Eng. Chem. Res.* **2005**, *44*, 1670–1676.
- (11) Huber, M. L.; Laesecke, A.; Perkins, R. A. Transport properties of dodecane. *Energy Fuels* **2004**, *18*, 968–975.
- (12) Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, ASTM Standard D 86-04b. *Book of Standards*, Vol. 05.01; American Society for Testing and Materials: West Conshohocken, PA, 2004.
- (13) *Handbook of Aviation Fuel Properties*; CRC Report No. 635; Coordinating Research Council (CRC): Alpharetta, GA, 2004.
- (14) Dean, L. E.; Shirley, L. A. Characteristics of RP-1 rocket propellant, 1957.
- (15) Edwards, T. “Kerosene” fuels for aerospace propulsion—Composition and properties. *AIAA 2002–3874, 38th AIAA/ASME/ASE/ASEE Joint Propulsion Conference and Exhibit*, Indianapolis, IN, July 2002.
- (16) Purchase Description, RP-1, Federal Business Opportunities, 2003 (<http://fs2.eps.gov/EPSTData/DLA/Synopses/12671/SP0600-03-R-0322/rp-1sol.pdf>).
- (17) Edwards, T. United States Air Force, Air Force Research Laboratory, Propulsion Directorate.
- (18) Magee, J. W.; Bruno, T. J.; Friend, D. G.; Huber, M. L.; Laesecke, A.; Lemmon, E. W.; McLinden, M. O.; Perkins, R. A.; Baranski, J.; Widegren, J. A. *Thermophysical Properties of RP-1, Phase I*; NIST-IR 6644; National Institute of Standards and Technology: Boulder, CO, 2006.
- (19) Bruno, T. J.; Andersen, P. C.; Widegren, J. Final Report, RP-1 Sample Composition Variability (MIPR NGWSPR00472412); Wright Laboratory Aero Propulsion and Power Directorate, Wright Patterson Air Force Base, 2004.

*Received for review* December 14, 2005  
*Revised manuscript received* March 6, 2006  
*Accepted* April 5, 2006

IE051394B